

Sodium-terminated zigzag graphene nanoribbon: A one-dimensional semimetal with a tilted Dirac cone

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Using first principles pseudopotential density functional theory calculations, we find that terminating zigzag graphene nanoribbons (ZGNR) with monovalent alkali atoms at a reduced concentration has a dramatic impact on their properties. In particular, using sodium atoms for the saturation of ZGNR edges at half the concentration of edge-carbon atoms make it a one dimensional, perfect semimetal, where the valance and conduction bands meet at only a single, Dirac-like point. Unlike pristine graphene, the Dirac-“cones” of Na-ZGNR is not symmetric with respect to wave vector, but rather it is tilted.

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After its realization as a stable monolayer structure [1], graphene has become a material of great interest for research in material science due to its impressive physical properties and the potential to tune them [2–6]. Pristine graphene is a zero-bandgap (perfect) semimetal. The conduction and valance bands of graphene meet linearly at six distinct points (Dirac-points) of first Brillouin zone, and are in the form of symmetric cones at the Fermi level [7]. Long and thin strips of graphene, known as graphene nanoribbons (GNR), are semiconducting and they have been experimentally realized with smooth edges and a range of widths down to sub 10 nm scale [8, 9]. As a special class, zigzag-edged GNRs (ZGNR) have width dependent energy band gaps, and are also expected to present edge localized spin states [10–14]. These localized spin states are ferromagnetically ordered at each edge and they are antiferromagnetically coupled to each other [15].

In computational studies of ZGNRs, to facilitate mechanical stability of the structure, the edges are usually terminated with hydrogen atoms, which lowers the values of its energy band gap and the induced magnetic moments of the edges. To manipulate the electronic properties of ZGNRs, modification [16, 17] and functionalization [18] of edges and producing defects, doping [19–22] and absorption [23–25] of atoms or molecules on ZGNRs have been extensively studied. For instance, recent studies [26, 27] have shown ways to obtain half-metallic ZGNRs.

In this letter we report that edge saturation of ZGNRs with Na atoms at a specific concentration makes them a zero-gap one dimensional semimetal with an asymmetric linear energy dispersion around the Fermi level. That corresponds to a Dirac cone similar to pristine two dimensional (2D) graphene [7], however, with a tilted form. Similar to hydrogenization of the edges, Na atoms saturates the dangling bonds of edge carbon atoms, and modify the local magnetic moment magnitudes and change the electronic band structure.

Geometry optimizations of bare and Na-terminated

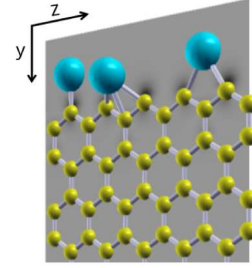


FIG. 1: (Color online) Schematic representation of various binding geometries of Na atoms to a ZGNR edge. From left to right: top in-plane (TI), bridge off-plane (BO), bridge in-plane (BI).

ZGNRs and calculations of their magnetic and electric properties were performed using the SIESTA package [28] based on density functional theory (DFT) [29]. We have used generalized gradient approximation (GGA) for the exchange and correlation potential as parameterized by Perdew, Burke and Ernzerhof [30]. For geometry optimizations, a local relaxation has been performed using the conjugate gradient algorithm and the convergence criteria of $0.04 \text{ eV} \times \text{\AA}^{-1}$ and 10^{-4} eV for the forces and total energies, respectively, in the self-consistency cycles. The electrostatic potentials were determined on a real-space grid with a mesh cutoff energy of 300 Ry. We make use of non-conserving Troullier Martins pseudopotentials [31] in the Kleinman Bylander factorized form [32] and a double- ζ polarized basis set composed of numerical atomic orbitals of finite range. The Brillouin zone has been sampled with (1,1,70) points within the Monkhorst-Pack k-point sampling scheme.

We have considered edge termination of n -ZGNRs (n denoting the number of zigzag rows in the ribbon) with monovalent atoms, i.e. H, Li, Na and K. Here we will report our results using Na terminated 9-ZGNR as a representative case. In Fig.1, different binding geometries of Na atoms to ZGNR determined after geometry optimizations are shown; these are, on top of an edge C atom,

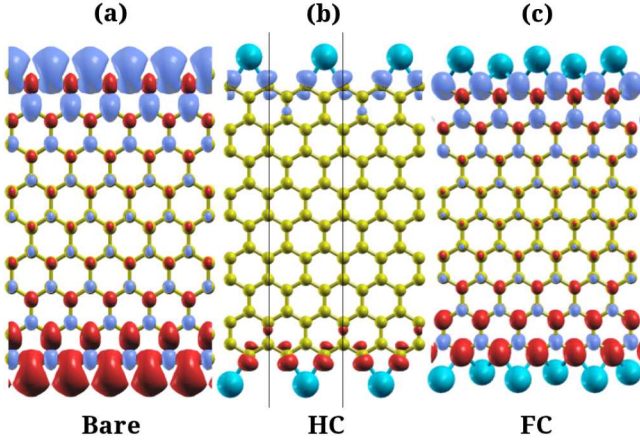


FIG. 2: (Color online) Relaxed geometric structure and isosurfaces of charge density difference of spin-up (\uparrow) and spin-down (\downarrow) states for 9-ZGNR; bare (a), and Na terminated at HC (b) and FC (c) concentrations. For all geometries, positive and negative values of the charge density difference is shown by red (dark) and blue (light) regions, respectively, for the same isosurface value of ± 0.0025 electrons/ \AA^3 .

in-plane with the ribbon (TI); bridge site of two edge C atoms, either off-plane (BO), or in plane (BI). Unlike H-termination, Na atoms prefer to bind at the bridge sites rather than the TI site; binding energy of a single Na atom at a BI site is 0.46 eV larger than that at a TI site. We considered two different concentrations of Na for saturation of the edges, full coverage (FC) where there are as many Na atoms as the edge C atoms, and half coverage (HC) where the Na atoms are bound to every other bridge site only (see Fig.2 for the unit cell of the ribbon and Na binding sites). In the HC case, equilibrium position of Na atoms is BI with a Na-C bond length of 2.33 \AA . In the FC case, however, due to their larger atomic size than H, neighboring Na atoms relax towards opposite directions at the BO sites. In this case, Na-C bond length and vertical distance of Na to the plane of ribbon are 2.35 \AA and 1.23 \AA respectively. Accordingly, the binding energy per Na atom reduces to 2.84 eV at FC from 2.91 eV at HC.

We calculated spin-dependent charge densities of the optimized structures and their difference ($\Delta\rho = \rho_{\uparrow} - \rho_{\downarrow}$). The characteristic edge-localized spin states of ZGNRs are preserved for both HC and FC concentrations of Na terminated 9-ZGNR (see Fig.2). Using Mulliken population analysis we have determined spin dependent atomic charges, total valance charge and the spin magnetic moments of the atoms. Total magnetic moments of the ribbons are found zero for all cases. As seen in the figure, there are no net induced magnetic moments on the Na atoms either. The penetration of the spin imbalance on the C atoms, $\Delta\rho$, toward the center of ribbons is considerably shorter for the HC case. Binding of Na atoms reduces the magnetic moments of the edge carbon

atoms from $\mu = 1.21 \mu_B$ to $\mu = 0.11 \mu_B$ for HC, and to $\mu = 0.28 \mu_B$ for FC. This magnetic moment reduction is comparable to the full hydrogenation of ZGNRs where edge carbon magnetic moments were reported as $\mu = 0.26 \mu_B$ [33]. When a Na atom binds to ZGNR edge, its valance charge is partially transferred to the ZGNR due to lower electronegativity of Na than C. At HC (FC) concentration, Na transfers 10% (15%) of its total valance charge. Correspondingly, total valance charge of each edge carbon atom of 9-ZGNR increases from 4.06 for bare ZGNR to 4.13 at HC and 4.20 at FC concentration.

In Fig. 3 we display the energy band diagram and density of states of Na terminated 9-ZGNR at HC and FC concentrations. Each case modifies the electronic properties of the ribbon differently. We calculate that bare 9-ZGNR is a direct gap semiconductor with $E_g = 0.70$ eV. Fully hydrogenated 9-ZGNR has a lower band gap of $E_g = 0.50$ eV, consistent with a previous report [34]. Similarly, 9-ZGNR terminated with Na at FC concentration has a reduced and slightly indirect band gap of $E_g = 0.44$ eV.

At HC concentration of Na termination the 9-ZGNR becomes a zero-gap semimetal with an interesting band structure. The valance and conduction bands intersect at a single point. In Fig.3(a), the Dirac-like point is located at $k_0 = 0.469 \text{ \AA}^{-1}$ in the first Brillouin zone ($k_z = 0.625 \text{ \AA}^{-1}$). The tilted Dirac cone is formed by a steep linear band crossing a relatively flat band at the Fermi level. These bands are mainly derived from carbon p_x and combination of carbon p_y and Na s orbitals, respectively. Since the present ribbon structure is one dimensional, the density of states (DOS) at the Fermi level does not vanish unlike 2D-graphene, and also, singularities characteristic to one-dimensional systems is evident in the DOS plot.

Energy band structures showing Dirac cones are quite rare. 2D-graphene is known for having symmetric and isotropic Dirac cones at corners of the first Brillouin zone. In this context, recently another two dimensional structure, which is an organic compound, has been reported as a unique material having a gapless band diagram and asymmetrical linear energy dispersion [35]. Na terminated ZGNR at HC concentration that we present in this study is a one dimensional member of this class of materials having tilted Dirac “cones”.

Around the Fermi level, E vs k relation can be approximated in the form,

$$E_{\lambda}(k) = w_0(k - k_0) + \lambda w |k - k_0| \quad (1)$$

where λ plays the role of band index (+1 for conduction, and -1 for valance band), $w = 2.517 \text{ eV} \times \text{\AA}$ and $w_0 = -2.277 \text{ eV} \times \text{\AA}$ are effective velocities. In this representation the w_0 parameter determines the degree of tilting of the Dirac cone. The slopes of the bands at the Fermi level are $w_0 + w = 0.240 \text{ eV} \times \text{\AA}$ and $w_0 - w = 4.794$

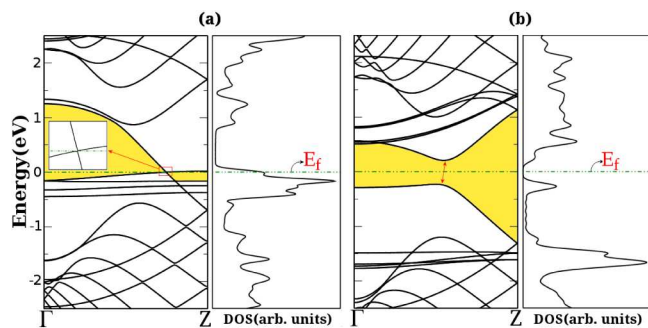


FIG. 3: (Color online) Band structures and density of states diagrams for 9-ZGNR. (a) HC, and (b) FC concentration of Na. The inset magnifies the tilted Dirac cone at the Fermi level for the HC case.

$\text{eV} \times \text{\AA}$, so that an asymmetry of about a factor of 20 in the slopes of the fermion and antifermion bands is present.

We find that the “tilted Dirac-cone” shaped band structure is quite robust with respect to the ribbon width and the approximations involved, such as exchange correlation functional being LDA or GGA. Using Li or K instead of Na also produces similar electronic structures, however, the valance and conduction bands intersect at slightly below or above the Fermi energies, respectively.

In summary, we have performed first-principles total energy calculations to investigate edge saturation of ZGNRs with Na atoms. Binding a Na atom to every other bridge site of the zigzag edge leads to formation of linear bands crossing at the Fermi level. To our knowledge, such tilted Dirac “cones” in a one dimensional material has not been reported before [36], and may find interesting spintronics applications. Such a one-dimensional semi-metal with charge carriers having high mobility is desirable for realization of nanoscale devices. Our preliminary results also show that edge saturation of ZGNRs with other monovalent alkali metals (Li and K) have similar effects, but those will be reported elsewhere.

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